Crystallization in a model glass:
influence of the boundary conditions

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Abstract

Using molecular dynamics calculations and the Voronoï tessellation, we study the evolution of the local structure of a soft-sphere glass versus temperature starting from the liquid phase at different quenching rates. This study is done for different sizes and for two different boundary conditions namely the usual cubic periodic boundary conditions and the isotropic hyperspherical boundary conditions for which the particles evolve on the surface of a hypersphere in four dimensions.

Our results show that for small system sizes, crystallization can indeed be induced by the cubic boundary conditions. On the other hand we show that finite size effects are more pronounced on the hypersphere and that crystallization is artificially inhibited even for large system sizes.

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When cooling a liquid down to low temperatures, what is the nature of the resulting solid phase ? The answer to this question in experimental studies or in numerical studies depends on how fast the liquid has been cooled down i.e. on the quenching rate. If the liquid is cooled faster than a critical rate, the resulting phase will be a glass otherwise the system will evolve towards the more stable crystal phase. The knowledge of this critical rate is very important especially in numerical studies of model glasses since crystallization effects should not bias the results at low temperature. Similarly to what had been done in a Lennard-Jones system [1] or in liquid sodium [2] we used the Voronoï cell statistics to determine this critical rate in a model soft-sphere glass [3]. Nevertheless in numerical studies due to computer time and memory limitations, one has to mimic macroscopic samples with the use of the so-called "boundary conditions". This is usually done by replicating a cubic box containing a few thousands of particles, for which the calculations will be explicitly done, in the 3 directions of space [4]. These boundary conditions are generally called periodic boundary conditions (PBC) and let us call this periodic space C_3. Obviously in this geometry the finite systems stay homogeneous but can bear a slight anisotropy. Therefore it is justified to address the question of the influence of this anisotropy on the crystallization of our model glass for which the ground state is a face-centered-cubic arrangement. In other words, do the cubic PBC favor crystallization ?

In this letter we investigate the influence of the boundary conditions and the system size on the evolution of the structure of a soft-sphere system during the quench with the use of classical molecular dynamics (MD) simulations. To distinguish an amorphous structure from a crystal or a partially crystallized system, we use the fraction of pentagonal faces of the Voronoï cell attached to each particle, which is an excellent tool to obtain this distinction [3]. As an alternative to the cubic PBC we use the "hypersphere boundary conditions" . This means that the MD simulations were performed by confining the system of soft-spheres to the surface S_3 of a hypersphere in four dimensions. This technique was used earlier for systems of charged particles [5], or fluids of hard-spheres [6] and Lennard-Jones particles [7]. The space S_3 (as well as C_3) is homogeneous, finite and non-Euclidean; but in addition, S_3

is isotropic therefore there is no preferential direction which could influence crystallization. Moreover for the calculation of long-range forces like Coulomb forces an advantage of using S_3 is a reduction of computer time by a factor 3-4 compared to the standard Ewald method [8]. Of course asymptotically for very large system sizes the results in C_3 and S_3 should converge.

Our results show that for small system sizes crystal nucleation occurs in C_3 while the system remains amorphous in S_3. This is coherent with previous results obtained for hard-sphere collections [6] and shows that the glass stability is, as desired, higher on the hypersphere. Nevertheless for larger systems we show that, compared to the asymptotic behavior which is as expected identical in C_3 and S_3 , the use of hyperspherical boundary conditions can artificially discourage crystal nucleation and therefore the value of the critical quenching rate can be underestimated. These results permit to shed new light on the influence of the widely used PBC on crystallization effects in model glasses and show the consequences of using isotropic boundary conditions in a curved three dimensional space such as S_3.

In our microcanonical MD simulations the particles interact via the repulsive potential proposed by Laird and Schober [9]:

$$U(r) = \epsilon(\frac{\sigma}{r})^6 + Ar^4 + B \ \ \text{for} \ \ r < 3\sigma \tag{1}$$
$$= 0 \ \ \text{for} \ \ r \geq 3\sigma$$

The constants A and B are chosen so that both the potential and the force are zero at the cut-off distance 3σ. To avoid reduced units, we use the values of Lennard-Jones argon for the mass m of the particles, as well as for ϵ and σ [10]. To integrate the equations of motion we use the Velocity Verlet algorithm [4] with a timestep $\Delta t = 2.5$ fs. To investigate the influence of the system size we use samples containing $N = 512$, 1000 and 5000 particles and to get better statistics we use either 10 independent configurations for $N = 512$ and 1000 or 2 configurations for $N = 5000$. For each system we start from a well equilibrated liquid sample at a temperature around 50K (well above the melting temperature $T_m \approx 23$K [11]) which is

then cooled down to zero temperature at two different quenching rates: $4.0 \times 10^{11} \mathrm{K/s}$ and $10^{11} \mathrm{K/s}$. The fastest quenching rate is close to the critical rate for which no crystallization should be observed after the quench while the second rate is smaller then this critical rate and therefore the system should be in a crystallized or partially crystallized state at the end of the cooling process [3]. To study the evolution of the structure as a function of temperature we save all along the quenching procedure configurations (positions and velocities) on which the Voronoï tessellation scheme is applied (it is worth noticing that no relaxation period has been considered). Once the Voronoï cell attached to each particle has been determined, we can calculate the fraction f_5 of pentagonal faces in the system. This is a good indicator of the degree of randomness (or on the other hand the degree of crystallization) since a large value of f_5 (typically around 0.45) is a sign of strong icosahedral local order characteristic of a glass phase, while a small value of f_5 (< 0.2) indicates crystal nucleation. Therefore we know for each sample if crystallization took place during the quench and we can determine at which temperature this crystallization started.

While MD simulations in C_3 are common and well established, we think it useful to give more details on the simulations in S_3. First of all concerning the density ρ, it is fixed and we use the value $\rho = N\sigma^3/V_{space} = 1$. In C_3 we use standard PBC with a rigid cubic box of edge length L ($V_{space} = L^3$) while in S_3 $V_{space} = 2\pi^2 R^3$ where R is the radius of the hypersphere. Fundamentally the volume fractions of the corresponding hard-sphere systems are not strictly equal in both spaces because one should take into account the curvature of the hard-spheres in the fourth dimension. Nevertheless a straightforward calculation shows that the relative error in S_3 is smaller than 5×10^{-3} % for the smallest system considered here ($N = 512$). Second let us detail a MD step in S_3. For convenience we chose to use the quaternion formalism [12] in order to describe the equations of motion in the four dimensional space. The unit quaternion $Q^i = (q_0^i, q_1^i, q_2^i, q_3^i)$ attached to particle i is defined by the set of q_k^is given by $q_k^i = x_k^i/R$, where the x_k^is are the coordinates of particle i in four dimensions, verifying $\sum_k (x_k^i)^2 = R^2$. We consider the potential $U(r)$ as being a function of the interparticle cartesian distance r in the four dimensional space. Thus the force F^i on

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particle i is a four dimensional vector, defined by the components f_k^i given by:

$$f_k^i = \sum_j \frac{(q_k^j - q_k^i)}{|Q^{ij}|} \left(\frac{\partial U}{\partial r}\right)_{r=r_{ij}} \tag{2}$$

where $|Q^{ij}|$ is related to the distance r_{ij} between particles i and j by $|Q^{ij}| = r_{ij}/R$. Next the force is projected on the three dimensional tangent space of particle i by calculating the quaternion product [12]

$$\Phi^i = \tilde{Q}^i F^i \tag{3}$$

where $\tilde{Q}^i = (q_0^i, -q_1^i, -q_2^i, -q_3^i)$ is the "conjugate" of Q^i. The acceleration of particle i in the three dimensional tangent space γ_k^i is obtained using the Newton's equations,

$$\gamma_k^i = \Phi_k^i/m \quad , \quad k = 1, 2, 3 \tag{4}$$

Once the acceleration has been calculated, the velocity is recovered using the standard Velocity Verlet scheme [4] and then the particle i can be moved to its new positions $Q^{i'}$ using

$$Q^{i'} = \frac{\delta Q^i Q^i}{|\delta Q^i|} \tag{5}$$

with $\delta Q^i = (1, \delta q_1^i, \delta q_2^i, \delta q_3^i)$ and $\delta q_k^i = (\Delta t v_k^i + (\Delta t^2/2)\gamma_k^i)/R$. The determination of the new positions completes the iteration and the process can be repeated as desired. In the scheme described above the dynamics is in fact performed in the four dimensional space with the constrain that the points should stay on the hypersphere. This implies that the first component of the force f_0^i, orthogonal to the hypersphere, is compensated by an adequate reaction force. We could have considered an alternative procedure consisting in staying on the hypersphere and considering forces between particles separated by the "geodesic" distance [5]. But, since only distances smaller than 3σ are considered here (for larger distances the potential is zero), the relative difference (due to the curvature of the hypersphere) between the cartesian distance and the geodesic distance remains smaller than a fraction of a percent for the smallest system considered here (512 particles). Therefore the quantitative

differences between the two approaches stay very small and in fact vanish in the infinitely large system limit.

Finally concerning the Voronoï tessellation in C_3, the scheme has been detailed elsewhere [13]. In S_3 the tessellation is done in the four dimensional space using the geodesic distance between particles [14]. For all the different samples and quenching rates, all the calculations have been made in parallel in S_3 and in C_3 in order to compare the effect of the boundary conditions on the final structure of the samples after the quench.

First we consider the fastest quenching rate $(4.0 \times 10^{11} \text{K/s})$. In Fig. 1 we report on the variation in C_3 and S_3 of f_5 versus the temperature for the three sizes considered in our study $(N = 512, 1000, 5000)$. It is worth recalling that the results have been averaged over several samples for the different values of N. The first observation concerns the asymptotic behavior obtained for the largest systems in both spaces: as expected this behavior is similar. Indeed if L or R increases, the description becomes closer to the one of the infinite system. As a general result, the finite size effects are more important for temperatures below the melting temperature. Moreover, if one excludes the case $N = 512$ in C_3, it appears that these finite size effects are more important in S_3 than in C_3. This is clearly visible when comparing the curves for $N = 5000$ and $N = 1000$ which are almost superimposed in C_3 and not in S_3. These finite size corrections act in opposite directions when comparing C_3 and S_3: in C_3 the small system sizes favor a small value of f_5 while in S_3 high values are favored. Indeed, the smaller the hypersphere, the higher f_5 i.e. the more the system is icosahedral. This can be explained by the fact that for $N = 120$ the ground state in S_3 is the "Polytope {3,3,5}" [15] made of dodecahedral Voronoï cells only, which means that for this ideal structure $f_5 = 1$. Therefore the more N decreases and comes closer to 120 the more the structure will resemble the Polytope {3,3,5} and the more f_5 will increase and tend towards 1. The fact that even for large systems f_5 remains greater than 0.43 at T=1K, indicates that no crystallization occurred during the quench and shows that the quenching rate is above the critical rate separating glass and crystal forming rates. Another point concerns the glass

transition which occurs around $T_g \approx 10.5$K [9] and which is reflected in a saturation of f_5 below T_g. This saturation is not obvious for $N = 512$ but is already visible for $N = 1000$ and is much more pronounced for $N = 5000$. Our results do not show a significant shift of T_g as a function of system size.

The huge difference between C_3 and S_3 is observed for $N = 512$. Indeed in C_3, for $N = 512$, Fig. 1 shows clearly a drop of f_5 below T_g with a saturation towards 0.36 at low temperature. Since these results have been averaged over ten samples, this indicates that some of the samples have crystallized during the quench. Snapshots of the structures at T=1K, confirm that three out of ten samples are crystals, one of them having a fraction of pentagonal faces smaller than 10^{-2} indicating an almost perfect crystalline character. These results are coherent with what has been observed in hard-sphere collections [6] and indicate that for small systems (a few hundred particles) the cubic PBC can indeed induce crystallization while the same systems remain "perfectly" amorphous with hyperspherical boundary conditions. Nevertheless this "encouragement" to crystal nucleation in C_3 already disappears for systems containing 1000 particles which is the size we have used in earlier studies [3].

In a second step we consider a quenching rate of 10^{11}K/s. This rate is smaller than the critical rate and therefore the structure after the quench should be crystalline. In Fig. 2 we show the variation of f_5 versus the temperature in S_3 and C_3 for $N = 1000$ and $N = 5000$. As expected the asymptotic behavior ($N = 5000$) is the same in both spaces: a drop of f_5 is observed below T_g indicating crystallization. In C_3 this effect is even more spectacular for the systems containing a thousand particles. In fact almost all of the ten samples considered in this study show a value of f_5 smaller than 0.2 at T=1K indicating that these samples have undergone crystallization. A look at snapshots of these crystalline structures does not show an obvious correlation between the axes of the periodic cubic box and the crystallographic directions. The fact that the samples containing $N = 1000$ particles exhibit an almost perfect crystalline character may be due to the difficulty to build extended defects in such small crystalline systems. This is not the case for the 5000 particles samples which may explain why these samples contain more defects and therefore show a higher value of f_5

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at small temperature ($f_5 \approx 0.35$). Nevertheless crystal nucleation occurred in S_3 and C_3 for $N = 5000$ and in C_3 for $N = 1000$. On the contrary the systems containing a thousand particles in S_3 do not show any sign of crystal nucleation. This indicates that for small system sizes the hyperspherical boundary conditions discourage *artificially* crystal nucleation. If the aim is to avoid crystallization then one should indeed work in S_3 with a relatively small system. On the other hand if one wants to determine the critical rate separating crystal forming rates from glass forming rates then the use of hyperspherical boundary conditions can lead to an underestimation of this rate. Indeed we quenched liquid samples containing 1000 particles at a rate of 4×10^{10}K/s and still we did not detect any sign of crystallization in S_3 even though the 5000-particles system crystallized. This is another example of the strong size effects in S_3: one needs to use a large system to get the correct results. On the contrary in C_3 the correct behavior is already obtained for systems containing 1000 particles.

In conclusion, we have used molecular dynamics simulations and the Voronoï tessellation to study the influence of the boundary conditions on the structure of the solid phase obtained after the quench of a soft-sphere system. This has been done for several system sizes ($512, 1000$ and 5000 particles) and for two different quenching rates close to the critical rate separating crystal from glass forming rates. To simulate a macroscopic sample we have used the usual cubic periodic boundary conditions (PBC) but also isotropic hyperspherical boundary conditions for which the particles are confined to the surface of a hypersphere in four dimensions. For the glass forming rate we show that for the smallest system size, the PBC can indeed induce crystal nucleation while the larger samples remain amorphous. This shows that caution should be used with the usual PBC when samples containing only a few hundred particles are considered. On the contrary for the crystal forming rate the results show that the hyperspherical boundary conditions can discourage *artificially* crystal nucleation even for samples containing thousand particles. On the one hand this is an advantage because no crystallization effects bias the results supposed to be obtained in a glass. On the other hand for a given system it leads to an underestimation of the critical quenching rate.

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Of course the asymptotic results obtained with 5000 particles are as expected similar using both boundary conditions but since it appears that the finite size effects are smaller when the usual PBC are used and even though the calculations on the hypersphere are slightly faster, our results indicate that in any case the correct behavior is obtained with the usual PBC for the 1000-particles samples. Of course this critical size depends on the interaction potential and should be re-determined for each different system.

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FIGURES

FIG. 1. Fraction of pentagonal faces, f_5, versus temperature in C_3 (open symbols) and S_3 (black symbols) for $N = 512$ (triangles), $N = 1000$ (squares) and $N = 5000$ (circles). The quenching rate is equal to 4×10^{11}K/s.

FIG. 2. Fraction of pentagonal faces, f_5, versus temperature in C_3: $N = 1000$ ($\blacktriangle$) and $N = 5000$ ($\bullet$). Idem in S_3: $N = 1000$ ($\blacklozenge$) and $N = 5000$ ($\blacksquare$). The quenching rate is equal to 10^{11}K/s.
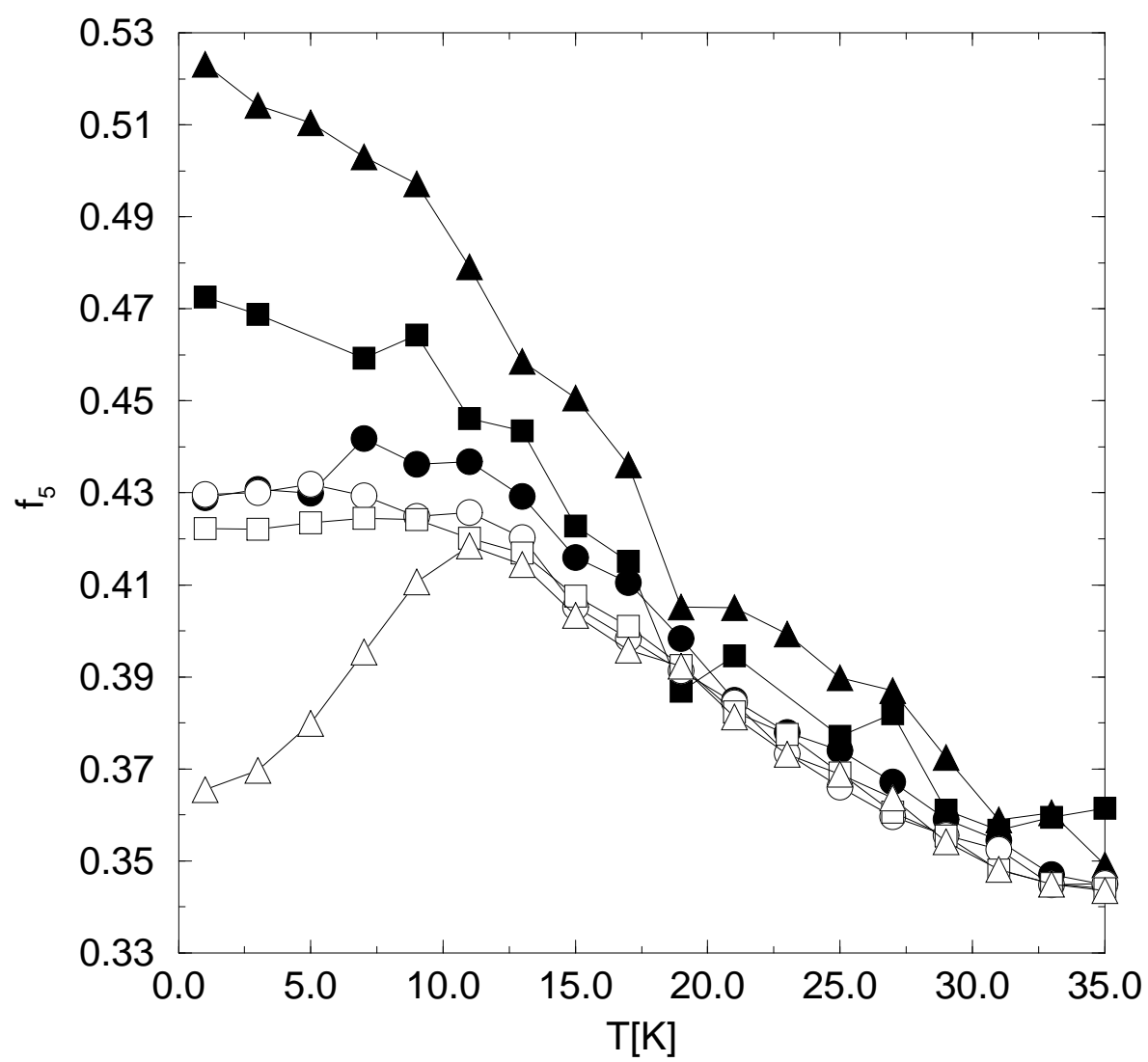
Fig. 1

Fig. 2